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Orientation relaxation of a water molecule

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A new interpretation of the low frequency (up to 1 THz) dielectric spectra of water based on the angular velocity autocorrelation function is proposed. We use Mori method to derive kinetic equations for the angular velocity autocorrelation function and obtain the angular velocity correlation time from the comparison of the theoretical result with the inelastic neutron scattering experiment. Using Hubbard relation we show that besides collective orientation relaxation, i.e. macroscopic dielectric relaxation, there is a single molecule orientation relaxation. It is much faster than the collective one and is displayed at the high frequency tail of the principal dielectric relaxation band. The analysis of the time dependence of the angular velocity autocorrelation function provides the evidence that the single-molecule relaxation is related to the molecules with partially broken H-bonds.

Water properties are an important subject of study for physics, chemistry, biology and different applied fields of natural science. Despite a great number of works devoted to liquid water there is no unified understanding of the experimental data. The existence of several types of intermolecular interactions leads to a complex associated structure of water. This structure is the cause of a number of abnormal properties of water. An important property of associating liquids is the cooperativity of molecular interactions due to hydrogen bonding. However, thermal motion as well as the competition between several types of intermolecular interactions, such as dipole-dipole and dispersion ones, strives to erode the spatial hydrogen bond network. This interplay determines temporal and spatial scales of cooperativity. It has been shown in recent molecular dynamics simulations that the strong interactions between neighboring water molecules lead to extended collective motions [1,2]. In the dielectric spectroscopy the cooperativity of water molecules is displayed by the principal relaxation band, reflecting the collective dipole orientation relaxation with the characteristic time τ_D, often called "Debye relaxation time" [3,4]. For example, water at the room temperature (25° C) has the relaxation time $\tau_D = 8.1$ ps, determined from the main peak of the imaginary part of the complex dielectric permittivity $\epsilon(\omega)$, occurring at about 18 GHz [5]. It should be pointed out that water has a near-ideal

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